California Environmental Protection Agency

Air Resources Board

SOP MLD 055

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF $PM_{2.5}$ MASS IN AMBIENT AIR BY GRAVIMETRIC ANALYSIS

Northern Laboratory Branch
Monitoring and Laboratory Division

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1. SCOPE

This document describes the methodology used by Monitoring and Laboratory Division (MLD) Inorganics Laboratory Section (ILS) staff to analyze the mass of $PM_{2.5}$ samples collected on Teflon filters.

2. SUMMARY OF METHOD

Individual Teflon filters (46.2 mm diameter) are weighed on an electronic microbalance before and after field sampling. Particulate matter less than 2.5 μm in diameter is collected from ambient air over a 24-hour period. $PM_{2.5}$ filters are sampled on three different types of samplers: 1. Andersen sequential sampler; 2. Rupprecht and Patashnick (R&P) single channel or sequential sampler; 3. Met One Instruments Speciation Air Sampling System (SASS™) low-volume sampler. The net difference between pre- and post-sampling filter weights is used to calculate the ambient air mass concentration. After post-weighing, all filters are archived; however, samples from the SASS™ sampler are stored for subsequent analysis.

3. INTERFERENCES

3.1 The potential effect of body moisture or oils contacting the filters is minimized by using non-serrated forceps to handle the filters at all times. This measure also moderates interference due to static electricity.

3.2 Teflon filters accumulate a surface electrical charge, which may affect filter weight. Static electricity is controlled by treating filters with a “Static Master” static charge neutralizer prior to weighing. Placement of filters on a “Static Master” unit is required for a minimum of 30 seconds before any filter can be weighed.

3.3 Moisture content can affect filter weight. Filters must be equilibrated for a minimum of 24 hours in a controlled environment prior to pre- and post-weighing. Per MLD’s ILS management, the balance room’s relative humidity must be maintained at a mean value range of 30-40 % and its air temperature must be maintained at a mean value range of 20.0-23.0 ^{o}C.

3.4 Airborne particulate can adversely affect accurate mass measurement of the filter. Filters undergoing conditioning should not be placed within an airflow path created by air conditioning ductwork, computer printers, or frequently opened doorways. Cleaning laboratory bench-tops and weighing areas daily, installing “sticky” floor mats at doorway entrances to the balance room and wearing clean lab coats over regular clothing can further minimize dust contamination.

4. APPARATUS

4.1 Sartorius MC5 electronic microbalance with a minimum resolution of 0.001 mg and a precision of ± 0.001 mg, supplied with a balance pan. The microbalance must be positioned on a vibration-damping balance support table and should be interfaced with the Laboratory Information Management System (LIMS) database system.

4.2 Calibration weights, utilized as Mass Reference Standards, should be non-corroding, range in weight from 100 mg to 200 mg, and be certified as traceable to NIST mass standards. Two sets are needed, one set as a working standard and one set as the primary standard. The weights should be ASTM Class 1 category with a tolerance of 0.025 mg.

4.3 Radioactive (alpha particle) Polonium-210 ("Static Master") antistatic strips for static charge neutralization. At least five strips are needed per balance.

4.4 Non-serrated forceps for handling filters.

4.5 Non-metallic, non-serrated forceps for handling weights.

4.6 Digital timer/stopwatch.

4.7 Filter: Teflon membrane, 46.2 mm diameter with a polypropylene support ring.

4.8 Filter support cassettes and covers.

4.9 Filter equilibration racks.

4.10 Relative humidity/temperature recorder.

4.11 NIST-certified hygrometer for calibration of relative humidity readings.

4.12 NIST-certified thermometer for calibration of temperature readings.

4.13 Light box.

4.14 Antistatic, nitrate-free, phosphate-free, sulfate-free, and powder free vinyl gloves.

4.15 Plastic petri-slide filter containers.

4.16 Zip-lock plastic bags, 6"x 9".

4.17 Disposable laboratory wipes.

4.18 Filter equilibration cabinets.

4.19 Metal filter-shipping canisters (supplied as an accessory equipment to Andersen FRM samplers).

5. BALANCE CALIBRATION PROCEDURE

5.1 Prior to any filter weighing session, the microbalance must be calibrated. First, check the microbalance base level and adjust as needed. To ensure maximum stability, the microbalance must remain on at all times.

5.2 **Internal Calibration**: Open the draft shield door for at least one minute to allow the balance weighing chamber to equilibrate to room temperature, then close the draft shield door. Press the "TARE" key when readout has stabilized to ensure zero-readout. The liquid crystal display (LCD) should display "0.000 mg". Press the "F1" key. The LCD should display "C". An acoustic signal indicates the end of the internal calibration.

5.3 **External Calibration**: Open the draft shield door. Place a 100 mg working reference standard calibration weight onto the microbalance pan with non-metallic forceps. Close the draft shield door. Record the date, temperature and relative humidity of the balance room, and mass readout in the quality control logbook assigned to the microbalance. Remove the calibration weight and tare the microbalance as described above. Enter the calibration data into LIMS and record the LIMS number assigned to the calibration session in the quality control logbook assigned to the microbalance. External calibration must be performed daily for each day that filters are pre-weighed and/or post-weighed.

6. FILTER INSPECTION AND STABILITY

6.1 For equilibration, the filters are transferred from their sealed manufacturer's packaging to a filter-handling container such as a plastic petri-slide. The filters are handled with non-serrated forceps. Lab personnel must wear vinyl gloves that are free of contaminant ions, powder-free, and anti-static when filters are being prepared for conditioning and weighing. Before any filter is placed in a filter-handling container, it must be inspected for defects. This is done by an examination of the filter on a "light table". A filter must be discarded if any defects are identified. Specific defects to look for are the following:

1. **Pinhole**—A small hole appearing as a distinct and obvious bright point of light when examined over a light table.

2. **Separation of ring**—Any separation or lack of seal between the filter and the filter support ring.

3. **Chaff or flashing**—Any extra material on the reinforcing ring or on the heat-seal area that would prevent an airtight seal during sampling.

4. **Loose material**—Any extra loose material or dirt particles on the filter.

5. **Discoloration**—Any obvious discoloration that might be evidence of contamination.

6. **Other**—A filter with any imperfection not described above, such as irregular surfaces or other results of poor workmanship.

6.2 **Lot Blanks**: Randomly select three filters as lot blanks from each new lot received and place in individual containers. Equilibrate the exposed filters in a filter equilibration cabinet in the Balance Room that allows air circulation, but still reduces extraneous airborne particles from settling on filters. Weigh lot blanks every 24 hours on a designated balance. The weighing process is described in Section 7. Record the lot number, filter number, mass, and dates of the lot blanks in the assigned quality control logbook. Once the mass difference between weighing is less than 0.015 mg for all three lot blanks, the filters have stabilized. Note the time taken from initial exposure of the filters to attainment of mass stability. This information is designated as the minimum equilibration period required before filters from the same lot can be pre-weighed and used for routine sampling. Once this minimum equilibration period is determined, the lot blanks become lab blanks which are set aside for long-term exposure in the same equilibration cabinet where routine samples, field blanks, and trip blanks are equilibrated prior to pre- or post-weighing.

6.3 Maintain an adequate supply of filters equilibrating so that the minimum equilibration period is always met before the filters are pre-weighed.

7. PRE-WEIGHING OF UNSAMPLED FILTERS

7.1 Record the relative humidity and temperature of the conditioning environment in the Balance Room in a quality control logbook assigned to the designated microbalance to be used for pre-weighing. Ensure that the temperature and the relative humidity of the Balance Room have remained (and are currently) within the allowable limits (see Section 3.3 for limits) throughout the preceding 24 hours. Also, make certain the selected filters have been conditioned for at least the minimum time needed to attain mass stability, as determined from the filter lot blanks.

7.2 Clean the microbalance weighing chamber with a fine brush, if necessary. Clean the surfaces near the microbalance with antistatic solution or disposable lab wipes moistened with isopropanol. Clean the forceps used for handling the mass reference weights and the filters prior to each weighing session. Ensure that all forceps in use are dry.

7.3 Perform an internal and external calibration of the microbalance as described in Section 5 prior to beginning the weighing session.

7.4 Prepare an appropriate number of CARB 24 hour - Field Sample Report (24-Hr Report) forms with site name(s) and barcode labels.

7.5 Obtain the appropriate filter support cassettes and metal covers. For filters being sent to monitoring sites using single-day Rupprecht and Patashnick samplers, use cassettes with a beveled inner edge on the top ring. All blue cassettes are for the R&P samplers. For filters being sent to monitoring sites using sequential Andersen samplers, use cassettes without the beveled top ring. For filters being sent to monitoring sites using SASS™ samplers, use petri-slides.

7.6 Create a batch by selecting up to ten of the conditioned unsampled filters. Using forceps, grip each filter only by the outer polypropylene support ring and place the filters

onto the static neutralizers. Allow each filter to remain on the static neutralizer for a minimum of 30 seconds prior to pre-weighing.

7.7 Place the 100 mg working standard on the balance pan and scan the CTL 100 barcode. Use the print key to transfer the weight reading after 30 seconds. Repeat these steps with the 200 mg working standard making sure to scan the CTL 200 barcode.

7.8 Scan the barcode number located on the 24-Hr Report form of the first filter of the batch to be pre-weighed.

7.9 Using forceps, place a filter on the balance pan and close the chamber. At the end of 30 seconds, press the "transmit/print" key on the balance to transfer the mass data to a local desktop computer. Record on the 24-Hr Report form the following:

1. Cassette identification (I.D.) number (each support cassette rim is marked with an I.D. number).

2. Pre-weight mass of the filter.

3. Date of pre-weight measurement.

4. Analyst's initials.

Place the weighed filter into the appropriate filter support cassette.

7.10 Repeat step 7.9 for subsequent filters. There must be a duplicate mass rate of ≥10%, so rescan and reweigh the first filter of the batch. If the original and duplicate mass values differ by ≥15 μg, check the two mass results, and reweigh the filter, if necessary. If the difference is still not ≤ 15 μg, consult with the lab supervisor. Transfer the duplicate mass to a local desktop computer.

7.11 After each duplicate weighing, alternately weigh the 100 mg and 200 mg working standards as described in Section 7.7.

7.12 Repeat steps 7.8 through 7.11 for subsequent batches of filters.

7.13 At the end of the weighing session, repeat step 7.7. After the last control has been transferred to the local computer, examine the worksheet data for errors and correct, if necessary.

7.14 Transfer data to LIMS.

7.15 When the set of filters have been weighed for R&P or Anderson samplers, snap the top of the cassette on, then place the protective metal covers on the bottom and top of the cassette. With an appropriate labeling system, designate whether or not a filter is a "field blank" or a "trip blank". If any filter(s) is labeled blank(s), make the appropriate notation on the corresponding 24-hr Report. If the filters are for a SASS™ sampler, place the top on the petri-slide and apply either a speciation "sample" label or a "field blank" label.

7.16 When pre-weighing for R&P or Andersen samplers is done, obtain a metal shipping canister for each site that filters were weighed for. Place the support cassettes containing the pre-weighed filter and the metal covers in the slots inside the metal filter shipping canister and screw on the cover. The 24-Hr Reports should be folded in a manner that easily identifies the site. Place these folded reports in a 6"x9" zip-lock bag and wrap the bag around the metal filter-shipping canister, securing with a large rubber band. Canisters are shipped to the site operator, delivered to a person in the building, or left for the site operator to pick up. Any canisters being shipped out are to be taken to the Stockroom where they will be shipped to the designated site.

7.17 When the pre-weighing for SASS™ samplers is done, deliver the filters contained in labeled petri-slides along with the corresponding custody/field data sheets to the bin in the speciation sample processing lab.

8. TRACKING DOCUMENTATION AND INSPECTION OF FIELD SAMPLES

8.1 Upon receipt of samples from the field, examine the Temperature Threshold Indicators inside the filter-shipping canister. These determine what receiving temperature is entered on the 24-Hr Reports with this canister. If both indicators have not turned blue, enter "<4". If the 5 ^{o}C indicator is blue, but the 26 ^{o}C indicator has not changed color, enter "4-25". If both have turned blue, enter ">25" and inform the supervisor. Also enter the current date, time, and your initials in the appropriate spaces for the "Sample Received at Lab" line for each of the 24-hr Reports.

8.2 Verify that each 24-Hr Report has a corresponding cassette. Inspect the condition of the exterior and interior walls of the canister for evidence of moisture accumulation on the filters.

8.3 Examine the Chain of Custody Record section of the 24-Hr Report. Each Report must have the following information and signatures:

	INFORMATION	SIGNATURES
1.	Date, time filter loaded onto sampler.	Site Operator
2.	Date, time filter removed from sampler.	Site Operator
3.	Date, time filter placed in freezer.	Site Operator
4.	Date, time, temperature conditions when filter shipped to lab.	Site Operator
5.	Date, time, temperature conditions when filter received.	Balance Room Staff

6.	Date, time, temperature conditions when filter begins equilibrating.	Balance Room Staff

If any of the above information and/or signatures are not available before login, these samples and their attached 24-Hr Reports are to be "flagged" and the site operator contacted to provide the missing information.

8.4 Remove each filter individually from the filter-shipping canisters. Detach the protective metal covers but leave each filter in its filter support cassette for identification purposes. Check the physical appearance of the filters, paying special attention to evidence of contamination and/or filter damage. Filters from SASS™ samplers will be found in the freezer in the speciation sample processing laboratory and will be in petri-slides. Custody/field data sheets for these samples will be in the bin on the laboratory workbench. These filters are handled the same as the R&P or Andersen filters.

8.5 If there is evidence of contamination and/or damage to the filter, make note of it in the "lab comments" section of the 24-Hr Report and write "INVALID" at the top of the report in red ink.

8.6 Remove the cassette top and allow each filter to condition on a designated rack for at least 24 hours. Assemble the 24-Hr Reports in such a manner as to facilitate login into the SQL*LIMS (LIMS) database.

8.7 All samples, whether designated as routine sample, field blank, or trip blank**,** will be logged into LIMS.

8.8 Each filter logged in using this program will generate a LIMS id number (i.e. 200091546). Write the LIMS id number on the 24-Hr Report.

8.9 Use a LIMS report to create a summary of $PM_{2.5}$ samples logged into LIMS for the selected date. The analyst reviews this report, checking for incomplete and flagged entries.

8.10 R&P and Andersen samples shipped and stored at a constant 4 ^{o}C or lower before equilibration must be weighed within 30 days of the sampling date. Samples shipped and stored at a constant range between 4 ^{o}C and 25 ^{o}C before equilibration must be weighed within 10 days of the sampling date. Any samples exceeding the time limit between sampling and post-weighing must be "flagged" and so noted on the matching 24-Hr Report and reported to the lab supervisor. The temperature of SASS™ samples received in the laboratory is monitored by the speciation program personnel. SASS™ samples must be weighed within 10 business days of receipt in the laboratory.

9. POST-WEIGHING OF FIELD SAMPLES

9.1 Generate a work list, and then divide the list into groups of ten with an assigned duplicate as the first sample in each group. After the samples have equilibrated for at least 24 hours, take the 24-Hr Reports of the samples that are to be post-weighed and affix matching barcodes labels on an equal number of petri-slides. Remove the sampled filters from the conditioning cabinet. Match up the filter cassette id numbers

with the correct 24-Hr Reports and petri-slides. Place them on the bench-top near the assigned microbalance.

9.2 Calibrate the microbalance described in Section 5. The lab blanks are weighed, and the I.D. number of each lab blank, its weight, the date of measurement, and initials of analyst are recorded in the quality control notebook. The average weight change for these lab blanks should not exceed 15 μg per day of exposure. If this limit is exceeded, consult with the lab supervisor before proceeding further.

9.3 Place the 100 mg working standard on the balance pan and scan the CTL 100 bar code. Use the print key to transfer the weight reading after 30 seconds. Repeat these steps with the 200 mg working standard making sure to scan the CTL 200 bar code.

9.4 Remove filters from the filter cassettes. Using forceps, grip each filter by the outer polypropylene support ring and place the filters onto static neutralizers. Allow each filter to remain on the static neutralizer for a minimum of 30 seconds prior to post-weighing.

9.5 Place a filter on the balance pan and close the chamber. At the end of 30 seconds, press the "transmit/print" key on the balance and the mass data will be transferred to a local desktop text file. Record the post-weight mass of the sample, date of post-weight measurement, and analyst's initials on the appropriate sample's 24-Hr Report.

9.6 Repeat steps 9.4 and 9.5 for subsequent filters. There must be a duplicate mass rate of ≥10% assigned on a work list. Since the first sample of each set of ten or less samples should be an assigned duplicate, rescan and reweigh the first filter of the batch. If the original and duplicate mass values differ by ≥15 μg, reweigh the filter. If the difference is still not ≤ 15 μg, consult with the lab supervisor.

9.7 Once the duplicate mass is transferred, alternately weigh the 100 mg and 200 mg working standard as described in section 9.3.

9.8 After the duplicate and check standard masses have been weighed, repeat steps 9.4 through 9.7 for subsequent batches of filters.

9.9 At the end of the weighing session, repeat step 9.3. After the 200 mg mass has been transferred, examine the data for any errors, check that the total number weighed is correct, and then transfer the data into LIMS.

9.10 After the data transfer into LIMS is complete, run the PM25-Post Weight Summary Report. Confirm that the percentage of duplicates to filters is not less than 10% and that there are no duplicates out of range. See section 9.6 for duplicate criteria and course of action.

9.11 Make sure field and/or trip blanks are within control. If not, reweigh filters.

9.12 Check the Primary/Collocated result section to see if the percent relative standard deviations (%RSD) are "OK". If not, check masses and reweigh, if necessary. If any of the above are still out, inform your supervisor.

9.13 If the $PM_{2.5}$ mass concentration exceeds 65 μg/m^3, notify the lab supervisor (calculations described in Section 10). If the mass variation between the pre-weight and post-weight of any blank filter is greater than 30 μg, "flag" that filter and notify the site operator and lab supervisor.

9.14 Place the weighed filter into a petri-slide, close tightly, and store at 4 °C for at least one year after sampling.

10. CALCULATIONS

10.1 The equation to calculate the mass of fine particulate matter collected on a Teflon filter is seen below:

$$M_{2.5} = (M_f - M_i) \times 10^3 \qquad \text{Equation 1}$$

where,

$M_{2.5}$ = total mass of fine particulate collected during sampling period (μg)
M_f = final mass of the conditioned filter after sample collection (mg)
M_i = initial mass of the conditioned filter before sample collection (mg)
10^3 = unit conversion factor for milligrams (mg) to micrograms (μg)

10.2 According to 40 CFR Part 50, Appendix L, $PM_{2.5}$ samplers are required to provide measurements of the total volume of ambient air passing through the sampler (V) in cubic meters at the actual temperatures and pressures measured during sampling. Use the following formula if V is not available directly from the sampler:

$$V = Q_{avg} \times t \times 10^{-3} \qquad \text{Equation 2}$$

where,

V = total sample volume (m^3)
Q_{avg} = average flow rate over the entire duration of the sampling period (L/min)
t = duration of sampling period (min)
10^{-3} = unit conversion factor for liters (L) into cubic meters (m^3)

10.3 The equation outlined below can be used to determine $PM_{2.5}$ mass concentration:

$$PM_{2.5} = \frac{M_{2.5}}{V} \qquad \text{Equation 3}$$

where,

$PM_{2.5}$ = mass concentration of $PM_{2.5}$ particulates (μg/m^3)
$M_{2.5}$ = total mass of fine particulate collected during sampling period (μg)
V = total volume of air sampled (m^3)

11. CALIBRATION CHECKS

11.1 **Temperature and Humidity Recorder Calibration**: Every quarter the temperature and humidity recorder (recorder) needs to be checked against a NIST traceable temperature and humidity instrument (standard). The standard is to be re-certified every year. Record the temperature and humidity readings about every two minutes from both the recorder and the standard at least ten times. Determine the averages of the temperature and humidity for both the recorder and the standard. Subtract the averages for the recorder from the averages for the standard. The differences should not be greater than ±2 ^{o}C for temperature and ±2 % for humidity. If the differences are greater than ±2, then adjust the recorder to be within range. Check the calibration again. These results are reported in the Inorganics quarterly quality control report.

11.2 **Calibration of Microbalance**: Every quarter the masses of the primary standards must be determined to check the performance of the microbalance. The primary standards are weighed on the balance and their average mass readings are compared to their certified mass values. If the average mass readings are not within ±0.003 mg of the certified masses, the balance must be re-calibrated; then the primary standards must be weighed again. If the difference in mass is still greater than ±0.003 mg, then the balance needs to be adjusted and re-certified. The primary standards are to be re-certified every year by an outside service.

11.3 Every year the microbalance must be re-certified.

12. REFERENCES

U.S. Environmental Protection Agency. *Quality Assurance Guidance Document 2.12, Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods*. November 1998.